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Waste Form Characteristics Report
CD-ROM Version

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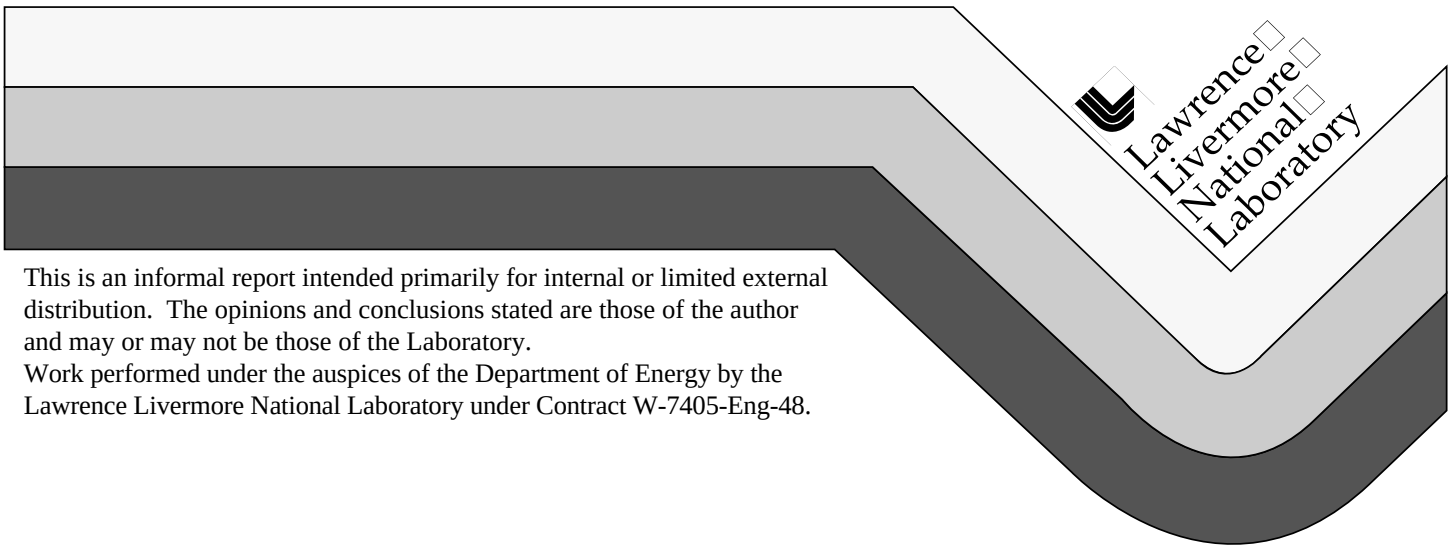

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Preface to CD-ROM Version

This CD-ROM version of the *Waste Form Characteristics Report* (WFCR) is a compilation of three versions of the document previously published in hard-copy form. To identify the version for a particular section, see the page footers. Note that the updates made in Version 1.3 superceded any changes made in Version 1.2. Thus, this version of the WFCR is actually a combination of the original text (Version 1.0) written in 1991 and published in 1994 and the text of Version 1.3 written in 1998.

Quality-assurance requirements and document guidelines have changed significantly since Versions 1.0 and 1.2 were published; consequently the qualified status of contents in those two versions has not been identified nor verified. The qualified status of contents in Version 1.3 are identified in Appendix A. This appendix applies to information appearing only in Version 1.3 sections of the document.

Sincere appreciation is extended to Karen L. Lew and Sharlene Markow for reformatting and preparing all versions of the document for publication on CD-ROM.

Ray Stout

December 1998

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Preface to Version 1.3

This version incorporates changes to 10 sections of the *Waste Form Characteristics Report*. Those sections changed are 2.1.3.1 Cladding Degradation; 2.1.3.2 UO_2 Oxidation in Fuel; 2.1.3.5 Dissolution Release from UO_2; 2.2.1.5 Fracture/Fragmentation Studies of Glass; 2.2.2.2 Dissolution Radionuclide Release from Glass; 2.2.2.3 Soluble-Precipitated/Colloidal Species from Glass; 3.2.2 Spent-Fuel Oxidation Models; 3.4.2 Spent-Fuel Dissolution Models; 3.5.1 Glass-Dissolution Experimental Parameters; and 3.5.2 Glass-Dissolution Models.

Eric Siegmann (CRWMS M&O) furnished section 2.1.3.1, and Brady Hanson (PNNL) provided section 2.1.3.2. William Bourcier was responsible for updating the glass properties and dissolution sections 2.2.1.5, 2.2.2.2, 2.2.2.3, 3.5.1, and 3.5.2. Edward J. Kansa updated section 3.2.2, which covers spent fuel-oxidation models. Steven A. Steward had the responsibility for the spent-fuel dissolution sections on data (2.1.3.5) and modeling (3.4.2). Ananda Wijesinghe provided the unsaturated test release modeling in section 3.4.2.

The evaluation of parameters for the models is based on test data obtained from previous and ongoing testing activities at Argonne National Laboratory, Chicago, Illinois; Lawrence Livermore National Laboratory, Livermore, California; and Pacific Northwest National Laboratories, Richland, Washington.

Sincere appreciation is extended to Steven A. Steward, who edited this update of the *Waste Form Characteristics Report*; to James C. Cunnane and J. Kevin McCoy, who technically reviewed it; and to Karen L. Lew, who edited the update and prepared it for submission and publication.

Ray B. Stout

July 1998

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Preface to Version 1.2

This version incorporates changes to several sections of the *Waste Form Characteristics Report*. Those sections changed are 2.1.3.5 Dissolution Release from UO_2; 3.2.2 Spent-Fuel Oxidation Models; 3.4.2 Spent-Fuel Dissolution Models; 3.5.1 Glass-Dissolution Experimental Parameters; and 3.5.2 Glass-Dissolution Models. These sections were also updated in Version 1.1 of the report (August 1996).

William Bourcier was responsible for updating the glass-dissolution sections 3.5.1 and 3.5.2. Edward J. Kansa updated section 3.2.2, which covers spent-fuel oxidation models. Steven A. Steward had the responsibility for the spent-fuel dissolution sections on data (2.1.3.5) and modeling (3.4.2).

The evaluation of parameters for the models is based on test data obtained from previous and ongoing testing activities at Argonne National Laboratory, Chicago, Illinois; Lawrence Livermore National Laboratory, Livermore, California; and Pacific Northwest National Laboratories, Richland, Washington.

Ray B. Stout

April 1997

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Preface to Version 1.0

Over the past several decades, sophisticated techniques have been developed to characterize the physical, thermal, chemical, mechanical, and radiological properties of nuclear radioactive waste form(s). (Here, "waste form" means the radioactive waste materials and any encapsulating or stabilizing matrix and is the definition provided by U.S. Nuclear Regulatory Commission in its regulation of Title 10 CFR 60.) Much of the early characterization was for design, operational efficiency, and safety of nuclear power plants. More recently, characterization activities have been directed at the design problem of safely emplacing radioactive waste form(s) in a suitable geological repository. The emplacement problem entails the teamwork of people from different technical disciplines, and the data exchange interfaces among the different technical personnel is of the utmost importance for an effective, efficient, and safe repository design.

With this need in mind, a preliminary data source of waste form characteristics has been assembled. Most of the data was taken from the open literature. The remaining data were summarized, in a preliminary form, from early results of ongoing waste-form-testing and model-development activities. In assembling the data, the intention has been to address waste-form-related informational needs for the wide variety of technical specialists that are part of a repository-design team. Care has been taken not to impose any limits or restrictions on waste-form response before the repository-design process because only an overall design analysis or performance assessment of the waste repository system can optimize the potential design trade-off options that satisfy requirements of a geologic repository containing radioactive waste form(s).

Because this is the first version of this waste form characteristics report, comments are expected and welcomed and other input from users, potential users, and others who are interested in waste form information is requested. In this way, the waste-form informational needs of the different technical specialists performing the design tasks for a repository can be met. It is anticipated that this report will be updated annually with new results from testing and model-development activities as well as with responses to the additional informational needs noted by users. Some deficiencies in data form and data needs have been identified and will be addressed in future revisions.

The accumulation of data was greatly facilitated because of the cooperation, interest, and esprit de corps of the following individuals, all of whom are graciously acknowledged and thanked: Karl Notz, Robert Einziger, Charles Wilson, Walter Gray, Harry Smith, Steve Marschman, Andrew Luksic, George Mellinger, John Bates, Les Jardine, Son Nguyen, Homer Weed, Knud Pedersen, Gregory Gdowski, Richard Van Konynenburg, William Bourcier, Carol Bruton, Stan Prussin, Andrew Zolnay, David Stahl, Richard Morissette, and Diane Harrison-Giesler. In addition, we extend a special thanks to William O'Connell for his helpful and meaningful review; Robert Day for his relentless pursuance of numerous corrections and resolution of review comments; and finally, to Sue Garber, for the fantastic job, performed with a smile, of putting the pieces together (again and again).

Ray B. Stout

Herman R. Leider

October 1991

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Abbreviations and Acronyms

AEM	analytical electron microscopy
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
BWR	boiling-water reactor
DHC	delayed hydride cracking
DIW	deionized distilled water
DTN	data-tracking number
DWPF	defense waste-processing facility
EDS	energy-dispersive spectroscopy
EELS	electron-energy-loss spectroscopy
EF	error factor
HBR	H. B. Robinson
HLW	high-level waste
LWR	light-water reactor
MWd	megawatt day
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
NNWSI	Nevada Nuclear Waste Site Investigations
NRC	Nuclear Regulatory Commission
ODB	oven drybath
O/M	oxygen-to-metal
PA	performance assessment
PNNL	Pacific Northwest National Laboratory
PWR	pressurized-water reactor
QA	quality assurance
RMS	root mean square
SIMS	secondary ion mass spectroscopy
S/V	surface/volume
SA/V	surface area/volume
SCCTP	substantially complete containment time period
SEM	scanning electron microscopy

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SNF	spent nuclear fuel
SPFT	single-path, flow-through
SRM	standard reference material
SS	stainless steel
TDMS	Technical Data Management System
TGA	thermal gravimetric analysis
TP	Turkey Point
TSPA	total system performance assessments
TSPA-VA	total system performance assessment–viability assessment
WFCR	*Waste Form Characteristics Report*
WP	waste package
WPA	waste-package assemblage
WPDD	Waste Package Development Department
XRD	X-ray powder diffraction
XRF	X-ray florescence
YMP	Yucca Mountain Site Characterization Project

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Executive Summary

This *Waste Form Characteristics Report* (WFCR) update, Version 1.3, incorporates substantial additions and changes to following 10 sections of the WFCR:

2.1.3.1 Cladding Degradation
2.1.3.2 UO_2 Oxidation in Fuel
2.1.3.5 Dissolution Release from UO_2
2.2.1.5 Fracture /Fragmentation Studies of Glass
2.2.2.2 Dissolution Radionuclide Release from Glass
2.2.2.3 Soluble-Precipitated/Colloidal Species from Glass
3.2.2 Spent-Fuel Oxidation Models
3.4.2 Spent-Fuel Dissolution Models
3.5.1 Glass Dissolution Experimental Parameters
3.5.2 Glass Dissolution Models

Section 2.1 includes accumulated data for spent-fuel waste forms. Section 2.1.3.1 on cladding failure describes process models for strain failure, delayed hydride cracking, and mechanical failure from rock drops. Also included is a discussion of as-received fuel with deteriorated cladding or fuel that is made with stainless-steel cladding that is expected to fail soon after the waste package (WP) fails. This section is considered preliminary and has been reproduced with minor modifications from Section 2.7.2 of the *Waste Form Degradation and Radionuclide Mobilization Preliminary Total System Performance Assessment*. Additional experimental and model-development efforts are necessary to substantiate the use of Zircaloy™ cladding as a barrier.

Experimental results of the thermogravimetric analysis (TGA) and oxidation drybath (ODB) spent-fuel–oxidation studies are in Section 2.1.3.2. These data provide the results of the oxidation studies, including the burnup and post-oxidation analyses performed. Detailed oxidation curves (oxygen-to-metal ratio as a function of time at operating temperature) for individual samples are included.

Spent-fuel dissolution and subsequent transport processes in groundwater are generally considered to be the main routes by which radionuclides could be released from a geological repository. Laboratory testing of the behavior of spent fuel under the conditions expected in a repository provides the information necessary to determine the magnitude of the potential radionuclide source term at the boundary of the fuel's cladding. Dissolution (leach) and release-rate tests of spent fuel and uranium dioxide (UO_2) are the most important aqueous data-collection activities in spent-fuel waste-form testing. Section 2.1.3.5 summarizes the available Yucca Mountain Site Characterization Project (YMP) spent-fuel and unirradiated-uranium–oxide dissolution and release data. The three dissolution activities (i.e., saturated [semi-static], flow-through, and unsaturated [drip] tests) have been separated, based on the different technical techniques involved in conducting each type of experiment. The intrinsic UO_2 dissolution rate sets an upper bound on the aqueous radionuclide release rate, even if the fuel is substantially degraded by other processes such as oxidation. Dissolution responses are provided, based on limited data, for spent fuel that is substantially degraded to other oxidation states. In scenarios for the potential geological repository, it is assumed that the

cladding has failed, and water as vapor or liquid contacts the fuel. Drip tests that simulate the unsaturated and oxidizing conditions expected at the proposed repository site have provided data to evaluate the long-term behavior of spent nuclear fuel.

Section 2.2 includes accumulated data for glass waste forms. Section 2.2.1.5 documents the recommended values of glass surface area to be used in estimating glass-alteration rates in the total system performance—viability assessment (TSPA-VA) modeling work. Unsaturated (drip) tests have been in progress since the mid-1980s. The tests using actinide- and technetium-doped Savannah River Site 165 glass are termed the N2 Test Series. Tests with a West Valley Demonstration Project former reference glass (ATM-10) are termed the N3 Test Series. Drip tests are designed to replicate the synergistic interactions among waste glass, repository groundwater, water vapor, and sensitized 304L stainless steel in the proposed geological repository. The information provided in Section 2.2.2.2 includes long-term data relevant to glass reaction under conditions anticipated for an unsaturated repository. Measurements obtained from each test series include the following:

Rate of glass reaction and radionuclide release as a function of time

Description of the distribution of radionuclides in solution (i.e., dissolved in solution, associated with colloidal material, or sorbed onto metal components of the test)

Monitoring of the interactions among the various components in the test

Ultimately, the results from these tests will be used to formulate and validate source terms of models used in WP performance assessment codes. Section 2.2.2.3 includes a brief description of the colloidal particle analysis of data from the unsaturated tests on waste glass reported in Section 2.2.2.2.

Section 3 contains descriptions of models for the responses of spent fuel and glass waste forms. Section 3.2.2 comprises a discussion of the oxidation-response model that was developed for the two phase-transitions $UO_2 \rightarrow U_4O_9$ and $U_4O_9 \rightarrow U_3O_8$, and for the model predictions for the geological repository. Because of the higher potential risk associated with the U_3O_8 phase, its modeling-phase transformation is emphasized. Arrhenius kinetic parameters for both phase transformations were obtained from a set of thermogravimetric analysis (TGA) experiments The two phase-formation models gave reasonable responses when compared with an independent set of experimental data. The oxidation history of the oven drybath (ODB) experiments could be explained by an envelope of various sizes of UO_2 grains. There is a focus on new material concerning the formation of U_3O_8. Although it has been predicted that burnup would be a very important property in spent-fuel oxidation, only recently has experimental evidence been obtained verifying this theoretical prediction. In the model, the activation energy for the phase transformation $U_4O_9 \rightarrow U_3O_8$, varies linearly with burnup. Experimental evidence shows that, for burnups greater than ~40 MWd/kgU, UO_2 grains undergo major restructuring to a much finer and more porous structure in the rim region of spent-fuel pellets.

Modeling of the aqueous dissolution- and release-rate responses of uranium oxide spent-fuel waste forms is described in Section 3.4.2. The derivation of dissolution-rate function forms is in Section 3.4.2.2. The previous nonequilibrium, thermodynamic model for dissolution rate (WFCR, Version 1.2) has been extended to include surface chemisorption effects. The surface chemisorption phenomenon is represented by the well-known Tempkin isotherm. This extension provides the theoretical basis for function forms used to regress the existing experimental data. Additional model development for radiolysis effects is in progress, but is not included at this revision. In Section 3.4.2.3, numerical regression analyses,

using various dissolution-rate functions are discussed. The incorporation of available new data has not changed the previous model significantly. The regression of the existing data to a dissolution-rate model suggested by outside experts has a small R-square–value (R^2) measure relative to the R^2 of the nonequilibrium, thermodynamic model. In Section 3.4.2.4, the aqueous release-rate modeling approach has not been changed. It has, however, been used as a basis to evaluate film concentrations of radionuclides in the alteration layers with data from the unsaturated drip tests. This film analysis and values of the film concentrations are discussed in Section 3.4.2.5.

The topic of Section 3.5.1 is experimental parameters and data as a basis for glass waste-form–dissolution models. These parameters include exposed glass surface area; solution chemistry, including pH and dissolved iron; temperature; and glass radionuclide content. To provide a context with which to place the parameters, a succinct summary of the fundamental rate equations in the model is included. More information on the model and its development is presented in Section 3.5.2 on dissolution models.

A chemical model of glass corrosion is used in Section 3.5.2 to predict the rates of release of radionuclides from borosilicate glass waste forms in a geological repository. The model is employed to calculate the rate of degradation of the glass and also to predict the effects of chemical interactions between the glass and repository materials (e.g., spent fuel, canister and container materials, backfill, cements, grouts). Coupling between the degradation processes affecting all these materials is expected.